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World Intellectual Property Organization (WIPO) - Geneva, Switzerland
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1378602

THE UNITED STATES OF AMERICA

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United States Patent and Trademark Office

October 14, 2005

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APPLICATION NUMBER: 60/524,965

FILING DATE: *November 25, 2003*

RELATED PCT APPLICATION NUMBER: *PCT/US04/39575*



Certified by

Under Secretary of Commerce
for Intellectual Property
and Director of the United States
Patent and Trademark Office

PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

Express Mail Label No. ER 644522055 US

| INVENTOR(S) | | | | |
|---|------------------------|---|--|--|
| Given Name (first and middle [if any]) | Family Name or Surname | Residence (City and either State or Foreign Country) | | |
| Paul Pei | Imhoff Chiu | Newark, Delaware Hockessin, Delaware | | |
| Additional inventors are being named on the _____ separately numbered sheets attached hereto | | | | |
| TITLE OF THE INVENTION (500 characters max) | | | | |
| PARTITIONING GAS TRACER TESTS FOR MEASUREMENT OF WATER IN MUNICIPAL SOLID WASTE | | | | |
| Direct all correspondence to: CORRESPONDENCE ADDRESS | | | | |
| <input checked="" type="checkbox"/> Customer Number: 23416 | | | | |
| OR Customer Number | | | | |
| <input type="checkbox"/> Firm or Individual Name | | | | |
| Address | | | | |
| City | | State | Zip | |
| Country | | Telephone | Fax | |
| ENCLOSED APPLICATION PARTS (check all that apply) | | | | |
| <input checked="" type="checkbox"/> Specification Number of Pages | | 36 | <input type="checkbox"/> CD(s), Number | |
| <input checked="" type="checkbox"/> Drawing(s) Number of Sheets | | 4 | <input type="checkbox"/> Other | |
| <input type="checkbox"/> Application Data Sheet. See 37 CFR 1.76 | | (specify): | | |
| METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT | | | | |
| <input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. | | | | |
| <input checked="" type="checkbox"/> A check or money order is enclosed to cover the filing fees. | | | | |
| <input checked="" type="checkbox"/> The Director is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number: 03-2775 | | | | |
| <input type="checkbox"/> Payment by credit card. Form PTO-2038 is attached. | | | | |
| FILING FEE AMOUNT (\$) 80.00 | | | | |
| The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government. | | | | |
| <input type="checkbox"/> No <input checked="" type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: U.S. Environmental Protection Agency - 99-0335-S4 | | | | |

Respectfully submitted,

SIGNATURE

TYPED OR
PRINTED NAME

TELEPHONE

Ashley I. Pezzner

(302) 658-9141

[Page 1 of 1]

Date November 25, 2003

REGISTRATION NO.
(if appropriate)

Docket Number:

35,646

00131-00345-US

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

22151 U.S. PTO
60/524965



Effective 10/01/2003. Patent fees are subject to annual revision.

C mplete if Known

| | |
|---------------------|----------------|
| Attorney Docket No. | 00131-00345-US |
|---------------------|----------------|

METHOD OF PAYMENT (check all that apply)☐ Deposit Account:

03-2775

Connolly Bove Lodge & Hutz LLP

The Director is authorized to: (check all that apply)

| | |
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| Charge fee(s) indicated below | <input checked="" type="checkbox"/> Credit any overpayments |
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☒ Charge any additional fee(s) during the pendency of this application

☐ Charge fee(s) indicated below, except for the filing fee to the above-identified deposit account.

FEE CALCULATION

1. BASIC FILING FEE

| | Large Entlty | Small Entlty |
|-------------------------|--|--|
| 1. Ownership | 100% owned by a single owner | Owned by multiple owners |
| 2. Control | Control is held by the owner | Control is shared among owners |
| 3. Liability | Owner is personally liable for the company's debts | Owners are not personally liable for the company's debts |
| 4. Taxation | Company is taxed as a sole proprietorship | Company is taxed as a corporation |
| 5. Financing | Financing is limited to the owner's personal funds | Financing is available from multiple sources |
| 6. Growth | Growth is limited by the owner's resources | Growth is not limited by the owner's resources |
| 7. Exit Strategy | Exit strategy is limited to the owner's personal funds | Exit strategy is available from multiple sources |

| Fee Code | Fee (\$) | Fee Code | Fee (\$) | Fee Description | Fee Paid |
|----------|----------|----------|----------|------------------------|----------|
| 1001 | 770 | 2001 | 385 | Utility filing fee | |
| 1002 | 340 | 2002 | 170 | Design filing fee | |
| 1003 | 530 | 2003 | 265 | Plant filing fee | |
| 1004 | 770 | 2004 | 385 | Reissue filing fee | |
| 1005 | 160 | 2005 | 80 | Provisional filing fee | 80.00 |

| | | |
|---------------------|-------------|--------------|
| SUBTOTAL (1) | (\$) | 80.00 |
|---------------------|-------------|--------------|

2. EXTRA CLAIM FEES FOR UTILITY AND REISSUE

| | | | Extra Claims | | Fee from below | | Fee Paid |
|-----------------------|----------------------|-----|----------------------|---|----------------------|---|----------------------|
| Total Claims | <input type="text"/> | ..* | <input type="text"/> | x | <input type="text"/> | = | <input type="text"/> |
| Independent Claims | <input type="text"/> | ..* | <input type="text"/> | x | <input type="text"/> | = | <input type="text"/> |
| Multiple Dependent | | | | | <input type="text"/> | = | <input type="text"/> |

| Large Entity | Small Entity |
|---|--|
| <p>1. Revenue Recognition</p> <p>Large entities use the percentage of completion method for long-term contracts, recognizing revenue as work progresses. Small entities often use the cost of sales method, recognizing revenue only when the contract is completed.</p> | <p>1. Revenue Recognition</p> <p>Small entities typically use the cost of sales method for long-term contracts, recognizing revenue only when the contract is completed.</p> |
| <p>2. Inventory Valuation</p> <p>Large entities use FIFO (First In, First Out) for inventory valuation. Small entities may use LIFO (Last In, First Out) for tax purposes.</p> | <p>2. Inventory Valuation</p> <p>Small entities may use LIFO (Last In, First Out) for tax purposes.</p> |
| <p>3. Depreciation</p> <p>Large entities use MACRS (Modified Accelerated Cost Recovery System) for depreciation. Small entities may use straight-line depreciation.</p> | <p>3. Depreciation</p> <p>Small entities may use straight-line depreciation.</p> |
| <p>4. Bad Debt Expense</p> <p>Large entities use the percentage of sales method for bad debt expense. Small entities may use the direct write-off method.</p> | <p>4. Bad Debt Expense</p> <p>Small entities may use the direct write-off method.</p> |
| <p>5. Research and Development</p> <p>Large entities use the capitalization method for research and development costs. Small entities may use the expensing method.</p> | <p>5. Research and Development</p> <p>Small entities may use the expensing method.</p> |

| Fee Code | Fee (\$) | Fee Code | Fee (\$) | Fee Description |
|----------|----------|----------|----------|--|
| 1202 | 18 | 2202 | 9 | Claims in excess of 20 |
| 1201 | 86 | 2201 | 43 | Independent claims in excess of 3 |
| 1203 | 290 | 2203 | 145 | Multiple dependent claim, if not paid |
| 1204 | 86 | 2204 | 43 | ** Reissue independent claims over original patent |
| 1205 | 18 | 2205 | 9 | ** Reissue claims in excess of 20 and over original patent |

| | | |
|---------------------|-------------|-------------|
| SUBTOTAL (2) | (\$) | 0.00 |
|---------------------|-------------|-------------|

****or number previously paid, if greater; For Reissues, see above**

FEE CALCULATION (continued)

3. ADDITIONAL FEES

| Large Entity | Small Entity |
|--|--|
| <p>1. Revenue</p> <p>2. Cost of Sales</p> <p>3. Operating Expenses</p> <p>4. Income</p> <p>5. Assets</p> <p>6. Liabilities</p> <p>7. Equity</p> | <p>1. Revenue</p> <p>2. Cost of Sales</p> <p>3. Operating Expenses</p> <p>4. Income</p> <p>5. Assets</p> <p>6. Liabilities</p> <p>7. Equity</p> |

| Fee Code | Fee (\$) | Fee Code | Fee (\$) | Fee Description | Fee Paid |
|----------|----------|----------|----------|--|----------|
| 1051 | 130 | 2051 | 65 | Surcharge – late filing fee or oath | |
| 1052 | 50 | 2052 | 25 | Surcharge – late provisional filing fee or cover sheet. | |
| 1053 | 130 | 1053 | 130 | Non-English specification | |
| 1812 | 2,520 | 1812 | 2,520 | For filing a request for <i>ex parte</i> reexamination | |
| 1804 | 920* | 1804 | 920* | Requesting publication of SIR prior to Examiner action | |
| 1805 | 1,840* | 1805 | 1,840* | Requesting publication of SIR after Examiner action | |
| 1251 | 110 | 2251 | 55 | Extension for reply within first month | |
| 1252 | 420 | 2252 | 210 | Extension for reply within second month | |
| 1253 | 950 | 2253 | 475 | Extension for reply within third month | |
| 1254 | 1,480 | 2254 | 740 | Extension for reply within fourth month | |
| 1255 | 2,010 | 2255 | 1,005 | Extension for reply within fifth month | |
| 1401 | 330 | 2401 | 165 | Notice of Appeal | |
| 1402 | 330 | 2402 | 165 | Filing a brief in support of an appeal | |
| 1403 | 290 | 2403 | 145 | Request for oral hearing | |
| 1451 | 1,510 | 1451 | 1,510 | Petition to institute a public use proceeding | |
| 1452 | 110 | 2452 | 55 | Petition to revive – unavoidable | |
| 1453 | 1,330 | 2453 | 665 | Petition to revive - unintentional | |
| 1501 | 1,330 | 2501 | 665 | Utility issue fee (or reissue) | |
| 1502 | 480 | 2502 | 240 | Design issue fee | |
| 1503 | 640 | 2503 | 320 | Plant issue fee | |
| 1460 | 130 | 1460 | 130 | Petitions to the Commissioner | |
| 1807 | 50 | 1807 | 50 | Processing fee under 37 CFR 1.17(q) | |
| 1806 | 180 | 1806 | 180 | Submission of Information Disclosure Stmt | |
| 8021 | 40 | 8021 | 40 | Recording each patent assignment per property (times number of properties) | |
| 1809 | 770 | 2809 | 385 | Filing a submission after final rejection (37 CFR 1.129(a)) | |
| 1810 | 770 | 2810 | 385 | For each additional invention to be examined (37CFR 1.129(b)) | |
| 1801 | 770 | 2801 | 385 | Request for Continued Examination (RCE) | |
| 1802 | 900 | 1802 | 900 | Request for expedited examination of a design application | |

Other fee (specify)

*Reduced by Basic Filing Fee Paid

| | | |
|---------------------|-------------|-------------|
| SUBTOTAL (3) | (\$) | 0.00 |
|---------------------|-------------|-------------|

SUBMITTED BY

| | |
|-------------------|-------------------|
| Name (Print/Type) | Ashley I. Pezzner |
|-------------------|-------------------|

Registration No.
(Attorney/Agent)

35,646

(Complete (if applicable))

Telephone (302) 658-9141

Signature

Date _____


November 25, 2003

Certificate of Express Mailing Under 37 CFR 1.10

I hereby certify that this correspondence is being deposited with the United States Postal Service as Express Mail, Airbill No. ER 644522055 US in an envelope addressed to:

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on November 25, 2003
Date



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J. Lynn Ferry

Typed or printed name of person signing Certificate

Note: Each paper must have its own certificate of mailing, or this certificate must identify each submitted paper.

Application Data Sheet;
Provisional Application For Patent Cover Sheet;
Provisional Patent Application with four sheets of drawings;
Fee Transmittal for FY 2004;
Check in the amount of \$80.00; and
Return Postcard

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION FOR U.S. LETTERS PATENT

Title:

Partitioning Gas Tracer Tests for Measurement of Water in Municipal
Solid Waste

Inventors:

Paul T. Imhoff
Pei C. Chiu

Ashley I. Pezzner - 35,646
CONNOLLY BOVE LODGE & HUTZ LLP
P. O. Box 2207
Wilmington, Delaware 19899-2207
(302) 658-9141

Government Contract

[0001] United States Environmental Protection Agency has rights through a subcontract through the University of New Orleans (UNO) Urban Waste Management & Research Center: UNO Account No. 32-20-5188, Contract No. 99-0335-S4.

Background of the Invention

[0002] Landfills operated as bioreactors are designed to enhance rates of waste decomposition and methane production (Komilis, D.P.; Ham, R.K.; Stegmann, R. The effect of landfill design and operation practices on waste degradation behavior: A review. *Waste Management & Research* 1999, 17, 20--26). The acidogenic phase of waste decomposition is also shortened in bioreactor landfills, resulting in reduced leachable organic emissions and reduced costs for leachate treatment (Komilis, D.P.; Ham, R.K.; Stegmann, R. The effect of landfill design and operation practices on waste degradation behavior: A review. *Waste Management & Research* 1999, 17, 20--26). An additional benefit of rapid decomposition is that waste settlement and compaction occur over a shorter time period, which may allow landfill space to be reclaimed sooner.

[0003] A key component in the operation of almost all bioreactor landfills is the addition of water to maintain optimal moisture conditions for biodegradation of organic wastes (Reinhart, D.R.; Townsend, T.G. *Landfill Bioreactor Design and Operation*, Lewis Publishers: Boca Raton, 1998). Typically, leachate collected from the bottom of the landfill is recirculated to modify the moisture conditions. However, knowing how much leachate to recirculate and where to add it is problematic. Municipal solid waste is composed of a wide variety of materials, and the common practice of adding soil cover to

land-filled material each day results in significant layering and heterogeneity. This heterogeneity in turn causes water to short circuit and move preferentially in a landfill, a process that has been difficult to measure or model (Johnson, C.A.; Richner, G.A.; Vitvar, T.; Schittli, N.; Eberhard, M. Hydrological and geochemical factors affecting leachate composition in municipal solid waste incinerator bottom ash Part I: The hydrology of Landfill Lostorf, Switzerland. *Journal of Contaminant Hydrology* 1998, 33, 361--376; Guyonnet, D.; Didier-Guelorget, B.; Provost, G.; Feuillet, C. Accounting for water storage effects in landfill leachate modeling. *Waste Management & Research* 1998, 16, 285--295).

[0004] A robust technique is required to measure water within landfills for the complex conditions in these systems. Historically, methods for measuring water were borrowed from soil science, where gamma ray attenuation (neutron probe), the dielectric constant (time-domain reflectometry and capacitance sensors), electrical resistance (gypsum blocks), water pressure (tensiometer), and thermal properties (thermal conductivity probe) are measured to quantify water in the pore space. While these methods work very well in soils, they typically produce measurements of dubious accuracy in landfills. The primary reason is that each of these methods requires that the surrounding matrix of water and solid waste have well-defined radiologic, electrical, hydrologic, or thermal properties that are invariant with time. While this constraint is easy to satisfy in most soils, it is virtually impossible to satisfy in a landfill. For example, waste settlement within a landfill will alter the average pore size and hydraulic conductivity in the vicinity of any sampling probe. Because the bulk dielectric constant of solid waste is quite sensitive to porosity (Li, R.S.; Zeiss, C. In situ moisture content measurement in MSW landfills with TDR.

Environmental Engineering Science 2001, 18, 53--66), and since it is difficult to correct for such changes as settlement progresses, measurement devices that rely on the dielectric constant might yield biased results. Furthermore, the heterogeneous nature of solid waste means that the chemical composition of material next to a probe will be different depending on the probe's location. For methods that rely upon gamma attenuation or the dielectric constant, it is difficult to calibrate the instrument for an entire landfill, since the gamma ray attenuation coefficient and dielectric constant of the solid waste material vary in space. Time dependent changes in the ionic strength of water within the landfill will influence electrical resistivity measurements and may lead to biased results for measurements that rely on this property.

[0005] A second disadvantage encountered with all of the current technologies is that they provide point measurements. If the flow and distribution of water within a landfill were uniform, then several point measurements might be adequate. However, preferential flow is common and probably a dominant process in most landfills, significantly decreasing the value of point measurements. Measurements of water in volumes that are 1-50 m³ may be significantly more valuable for landfill managers and environmental regulators.

[0006] The invention is the application of a relatively old process for an entirely new use. The original process involves injecting multiple chemical tracers in an oil reservoir and then measuring their concentrations through time at selected sampling wells in the underground formation. One chemical tracer is inert and moves with the groundwater unimpeded. Other tracers have an affinity for the oil trapped within the subsurface. These

partitioning tracers partition into and out of the immobile oil and move at a slower relative speed than the inert tracer. The mean arrival times of the inert or conservative tracer and the partitioning tracers are computed at the sampling wells. This information is then used in a simple algebraic formula to compute the average fraction of the pore space filled with oil between the point of tracer injection and the sampling well.

In the last 7 years this technology was tested for a new application by environmental engineers. The tracers were injected and withdrawn from the subsurface to quantify the amount of residual oily waste in the soil, which is associated with prior contamination spills. More recently, the technology has been used by soil scientists to measure the amount of water within soils. In this case, the tracers are injected in the gas phase, with the conservative tracer moving with the mean gas velocity while the partitioning tracers partition into and out of immobile or slowly moving water. In this case, the tracer test is used to quantify the amount of water in the soil between the point of tracer injection and sample measurement.

[0007] In order to estimate the accuracy of partitioning tracer tests for measuring nonaqueous phase liquids in subsurface media, computational experiments were conducted in a hypothetical aquifer contaminated with nonaqueous phase liquids (Jin, M.; Butler, G.W.; Jackson, R.E.; Mariner, P.E.; Pickens, J.F.; Pope, G.A.; Brown, C.L.; McKinney, D.C. Sensitivity models and design protocol for partitioning tracer tests in alluvial aquifers. *Groundwater* 1997, 35, 964--972). The investigators concluded that the retardation factor should be between 1.2 and 4 in order to obtain the response curve of the partitioning tracer in a reasonable sampling period, and to ensure that good separation was achieved between

the conservative and partitioning tracers. Based on this study, similar constraints were later assumed to apply for partitioning gas tracer tests for the detection of nonaqueous phase liquids in the vadose zone (Whitley Jr., G.A.; McKinney, D.C.; Pope, G.A.; Rouse, B.A.; Deeds, N.E. Contaminated vadose zone characterization using partitioning gas tracers. *Journal of Environmental Engineering* 1999, 125, 574--582).

[0008] The current invention involves the application of this technology to a new use – the measurement of water in landfilled solid waste. The internal regions of landfills are extremely heterogeneous environments where the only reliable method for measuring water is to physically remove solid waste samples and make gravimetric measurements. Because water is often the limiting factor for degradation of solid waste materials, measuring it in various regions of a landfill has become an important problem. More recently, the U.S. Environmental Protection Agency and landfill owners have shown tremendous interest in operating landfills as bioreactors, where water is added in a controlled fashion to maintain optimal moisture conditions for solid waste degradation. Because physical sampling of the waste in situ is expensive and often impractical, the partitioning gas tracer technology offers tremendous promise.

Summary of the Invention

[0009] We have developed a new use for this technology, to measure water within landfills. At least two gas tracers are injected into a landfill. At least one tracer is nonreactive with landfill materials, while the second partitions into and out of water trapped within the pore space of the solid waste. Chromatographic separation of the tracers occurs between the point of tracer injection and tracer extraction because the second

partitioning tracer is retarded due to water in the landfill. The degree of tracer retardation can be used to determine the average fraction of the pore space filled with water in the volume sampled by the tracer gases. This volume may be small or large and depends on the locations of tracer injection and extraction; the sampling volume is comprised of all stream paths between the injection and extraction points that are sampled. The partitioning gas tracer test (PGTT) should not be affected by solid waste compaction or heterogeneity of the solid waste composition.

[00010] The invention differs from the previous applications of this technology as follows:

- (a) Water is measured in solid waste, not soil.
- (b) Solid waste contains a lot of water tightly bound in paper, food waste, etc.
Measuring water in this mixture is different from measuring water in soil.
- (c) Landfill temperatures can be significantly higher than that of groundwater or most soils.
- (d) Water within landfills is much different from water in soils. It has many dissolved salts and organics that may make application of the partitioning gas tracer technology challenging.
- (e) The solid waste within landfills is decomposing and generating methane and carbon dioxide. These gases are then collected from the landfill for some type of treatment. Thus, there is a natural generation of gas within landfills that does not exist within soils.

[00011] Brief Description of the Figures

[00012] Figure 1. Example breakthrough curve from tests to determine Henry's law constant.

[00013] Figure 2. Water content θ_w measured with PGTT versus gravimetrically determined θ_w . Error bars represent error associated with uncertainty in the gas flow rate measurements.

[00014] Figure 3. Change in Henry's law constant K_H for difluoromethane associated with the presence of three dissolved salts. Each line represents the effect of a single salt.

[00015] Figure 4. Error in water saturation S_w due to an error in Henry's law constant K_H for difluoromethane.

[00016] Detailed Description Of The Invention

[00017] Measuring water within landfills is an important operational requirement for bioreactor landfills. Existing in situ methods may be influenced by leachate composition and properties of the solid waste. The partitioning gas tracer test (PGTT) is a new technology. Our results indicate that PGTT results in unbiased estimates of water saturation, over the measured range of saturations from 10% to 39%. Our results indicate that the PGTT holds much promise for measuring water within municipal solid waste landfills.

[00018] Solid waste disposed of in landfills contains large pores associated with the voids between waste components and small pores within waste components. For example, paper

can be considered a porous medium, with pores on the order of microns in size. Water resides in both large voids and in small porous regions. Theoretically, PGTTs are capable of measuring water in both domains, assuming that sufficient time is allowed for the water-partitioning tracer to diffuse into and out of all water in the system and tracer detection limits are sufficiently small. More commonly, though, PGTTs may only measure the water residing in the most accessible domains of the solid waste, i.e., the larger voids.

[00019] In several recent investigations PGTTs were used to quantify the volumetric water content θ_w (volume of water/sample volume) or the water saturation S_w (volume of water/volume of pore space) in soils in laboratory columns (Deeds, N.E.; McKinney, D.C.; Pope, G.A.; Whitely Jr., G.A. Difluoromethane as partitioning tracer to estimate vadose water saturations. *Journal of Environmental Engineering* 1999, 125, 630--633; Brusseau, M.L.; Popovicova, J.; Silva, J.A.K. Characterizing gas-water interfacial and bulk-water partitioning for gas-phase transport of organic contaminants in unsaturated porous media. *Environmental Science & Technology* 1997, 31, 1645--1649), a large mesoscale apparatus (Nelson, N.T.; Brusseau, M.L.; Carlson, T.D.; Costanza, M.S.; Young, M.H.; Johnson, G.R.; Wierenga, P.J. A gas-phase partitioning tracer method for the in situ measurement of soil-water content. *Water Resources Research* 1999, 35, 3699--3707), and at a field site (Deeds, N.E.; Pope, G.A.; McKinney, D.C. Vadose zone characterization at a contaminated field site using partitioning interwell tracer technology. *Environmental Science & Technology* 1999, 33, 2745--2751). For the laboratory columns and mesoscale apparatus, S_w determined from the gas tracers were typically within 12% percent of S_w determined

by independent measurements. No independent measurement of S_w was available from the field site, but measured values were within expected ranges. Mass recoveries of the tracers in the field test ranged between 57-60%, since not all gases injected into the soil were extracted. However, it was not necessary to sample all tracer stream paths and collect all tracer mass. Instead, the only requirement was that the *same* stream paths were sampled for the partitioning and conservative tracers (Whitley Jr., G.A.; McKinney, D.C.; Pope, G.A.; Rouse, B.A.; Deeds, N.E. Contaminated vadose zone characterization using partitioning gas tracers. *Journal of Environmental Engineering* 1999, 125, 574--582).

[00020] Given the past success of the PGTT for measuring water in soils, a laboratory investigation was conducted to evaluate the utility of this technology for measuring water in municipal solid waste. Gas tracers were selected for a landfill environment, and PGTTs were conducted in municipal solid waste that was packed into laboratory columns. Tracer tests were used to quantify the utility of the technology over a range of volumetric water contents, and when the water was solute-free or a landfill leachate.

THEORY OF PARTITIONING GAS TRACER TEST

Tracer Partitioning and Transport

[00021] The basic theory behind PGTT is based upon the same principle used for chromatographic separation of chemicals: the mean travel velocity of a gaseous compound along a stream path is determined by the affinity of the compound for the immobile phase contacted along that path. If a tracer is nonreactive, it travels at the velocity of the bulk gas phase. If a tracer is reactive and partitions into an immobile phase along the stream path, the mean travel velocity will be a function of the gas phase velocity, the affinity of the

tracer for the immobile phase, and the amount of the immobile phase along the stream path.

[00022] Differences in the mean travel times of partitioning and conservative tracers were first used by researchers in petroleum engineering to determine the amount of residual oil within oil reservoirs (Cooke, C. E. *Method of determining fluid saturations in reservoirs*, U.S. Patent 3590923, 1971; Tomich, J.F.; Dalton, R.L.; Deans, H.A.; Shallenberger, L.K. Single-well tracer method to measure residual oil saturation. *Journal of Petroleum Technology* 1973, Feb., 211--218; Tang, J.S. Interwell tracer tests to determine residual oil saturation to waterflood at Judy Creek BHL "A" Pool. *Journal of Canadian Petroleum Technology* 1992, 31, 61--71). More recently the same principles were applied by hydrologists to determine the amount of water in the vadose zone (Deeds, N.E.; McKinney, D.C.; Pope, G.A.; Whitely Jr., G.A. Difluoromethane as partitioning tracer to estimate vadose water saturations. *Journal of Environmental Engineering* 1999, 125, 630--633; Brusseau, M.L.; Popovicova, J.; Silva, J.A.K. Characterizing gas-water interfacial and bulk-water partitioning for gas-phase transport of organic contaminants in unsaturated porous media. *Environmental Science & Technology* 1997, 31, 1645--1649). In each case investigators reasoned that the retardation factor R_f of a chemical tracer was related to tracer partitioning and the amount of immobile liquid (oil or water) present, where

$$R_f = \frac{\bar{v}_c}{\bar{v}_p} \quad (1)$$

and is the ratio of the mean travel velocity of a conservative tracer \bar{v}_c to the mean travel velocity of a partitioning tracer \bar{v}_p . Standard moment analysis of tracer breakthrough

curves was used to determine the mean travel velocities (Ptak, T.; Schmid, G. Dual-tracer transport experiments in a physically and chemically heterogeneous porous aquifer: Effective transport parameters and spatial variability. *Journal of Hydrology* 1996, 183, 117-138).

[00023] If a tracer travels in the gas phase within a landfill and if linear partitioning is assumed between a tracer and the immobile phases in the system, application of conservation of mass to tracer transport results in the following expression for R_f (Brusseau, M.L.; Popovicova, J.; Silva, J.A.K. Characterizing gas-water interfacial and bulk-water partitioning for gas-phase transport of organic contaminants in unsaturated porous media. *Environmental Science & Technology* 1997, 31, pps. 1645--1649)

$$R_f = 1 + \frac{S_w}{(1 - S_w)K_H} + \frac{\rho_b K_d}{n(1 - S_w)K_H} + \frac{K_{IA} A_{IA}}{n(1 - S_w)} \quad (2)$$

where K_H is the dimensionless Henry's law constant, the ratio of the concentration of the tracer in the gas phase to that in the water phase at equilibrium; ρ_b is the dry bulk density of the solid waste (ML^{-3}); K_d is the sorption coefficient for the tracer onto the solid waste (M^{-1}L^3); n is the porosity of the system, the volume of voids per unit bulk volume; K_{IA} is the adsorption coefficient for the gas-water interface phase, the ratio of the concentration of the tracer in the gas-water interface phase to that in the gas phase at equilibrium (L); and A_{IA} is the specific surface area of the gas-water interface, the interfacial area per unit bulk volume of the system (L). For landfills a tracer may be retarded because of partitioning into water, solid waste, or the gas-water interface. If nonaqueous phase liquids are present

in the landfill (e.g., motor oil, industrial solvents), partitioning into these fluid phases may also occur, although for now we neglect this possibility.

[00024] If the objective is to measure the amount of water in a prescribed volume of the land-filled material, the best partitioning tracer is one whose retardation is dominated by the bulk water in the system, such that sorption onto the solid waste and the gas-water interface are negligible in comparison. The ideal conservative tracer is one that has very little affinity for the solid and liquid phases in the system. For a partitioning tracer whose retardation is dominated by partitioning in the water, eq 2 can be rewritten as

$$R_f = 1 + \frac{S_w}{(1 - S_w)K_H} \quad (3)$$

If R_f is determined by the tracer breakthrough curves, the water saturation can be computed from eq. 3, assuming the appropriate Henry's law constant is known for the partitioning tracer.

[00025] The Henry's law constant is a key thermodynamic property that influences a compounds fate in the environment. Depending on the nature of an organic compound, K_H may be a function of temperature, pH, compound hydration, compound concentration, and the presence of additional substances in the aqueous phase, e.g., organic compounds, dissolved salts, suspended solids, dissolved organic matter, or surfactants (Staudinger, J.; Roberts, P.V. A Critical review of Henry's Law constants for environmental applications. *Critical Reviews in Environmental Science and Technology*, 1996, 26, 205--297). Landfill leachate typically contains dissolved organic matter; inorganic macrocomponents, such as Ca, Mg, SO_4^{2+} , and HCO_3^{-1} ; and small amounts of xenobiotic organic compounds

originating from household or industrial chemicals, such as hydrocarbons and chlorinated aliphatics (Christensen, T.H.; Kjeldsen, P.; Bjerg, P.L.; Jensen, D.L.; Christensen, J.B.; Baun, A.; Albrechtsen, H.-J.; Heron, G. Biogeochemistry of landfill leachate plumes. *Applied Geochemistry* 2001, 16, 659--718). The Henry's law constant for a partitioning tracer selected for a landfill environment must be minimally affected by these factors for typical leachate conditions.

[00026] While a PGTT is used to measure the water saturation, it is difficult to obtain independent measurements of S_w within solid waste to evaluate the accuracy of this technology. Typically, the wet-weight moisture content of the solid waste (mass of water/wet mass of solid waste) is determined by gravimetric measurements and is used to assess moisture content (Tchobanoglous, G.; Theisen, H.; Vigil, S. *Integrated Solid Waste Management, Engineering Principles and Management Issues*, McGraw-Hill, Inc.: New York, 1993). In a closed one-dimensional system in the laboratory, though, gas tracers can be used to measure the porosity of the solid waste as well as S_w . In this case the volume of the gas phase V_g that the tracers travel through is estimated from transport of the conservative tracer

$$V_g = \frac{Q_g X}{\bar{v}_c} \quad (4)$$

where Q_g is the volumetric flow rate of the gas injected into the system and X is the distance between the injection and extraction points. With S_w determined from eq. 3, the porosity of the system can be computed

$$n = \frac{V_g / (1 - S_w)}{V_t} \quad (5)$$

where V_t is the total volume of the experimental system which is known. The volumetric water content of the solid waste can then be calculated from $\theta_w = nS_w$. Because θ_w is easily determined from gravimetric measurements, a useful means of evaluating the accuracy of the PGTT under laboratory conditions is to compare θ_w determined from PGTT measurements with gravimetrically determined θ_w . This procedure was followed here. In the field, though, the system is not closed and V_t is unknown. In this case only S_w can be determined from a PGTT.

Time Moment Analysis

[00027] A time moment analysis is typically used to determine the retardation factor from the breakthrough curves of the two tracers (Ptak, T.; Schmid, G. Dual-tracer transport experiments in a physically and chemically heterogeneous porous aquifer: Effective transport parameters and spatial variability. *Journal of Hydrology* 1996, 183, 117-138).

The n th temporal moment is defined as

$$M_{n,t} = \int_0^{\infty} t^n C_g(x,t) dt \quad (6)$$

where C_g is the gas phase concentration of the solute measured at the point of tracer extraction and t is time. The mean or effective transport velocity of a gas phase tracer is then computed from

$$\bar{v} = \frac{X}{M_{1,t} / M_{0,t}} \quad (7)$$

where X is the distance between the injection and extraction points. The mean velocities of the tracers differ from each other, depending on the degree to which each tracer is retarded during transport. Using the measured travel velocities for the conservative and partitioning tracers, the retardation factor for the partitioning tracer is computed from eq. 1.

EXPERIMENTAL METHODS

Tracer Gas Selection

[00028] Two tracers are required for a PGTT: a conservative tracer that does not partition significantly into solids or liquids within landfills, and a partitioning tracer that partitions into the bulk water found in landfills, but has minimal affinity for the gas-water phase interface or the solid waste. These tracers must also be nontoxic, nonbiodegradable over the time period of the PGTT, easily detectable within the gas phase, and absent from landfill gas or found at only small concentrations within the gas phase.

[00029] Several gases may serve as conservative tracers within landfills including noble gases, such as neon, helium, and argon, and perfluorinated compounds, such as sulfur hexafluoride (SF₆) and carbon tetrafluoride (CF₄). Each of these gases has a low affinity for water (large K_H) and has negligible affinity for solid waste (small K_d) and the gas-water phase interface. These tracers also satisfy the other constraints listed above. In the examples helium was selected as the conservative tracer gas, and its properties are shown in Table 1.

| Table 1. Tracer gases selected for laboratory investigation. | Formula | Molecular Weight | K_H at 25°C (-) | Log n-Octanol/Water Partition Coefficient (-) | Concentration In Injection Gas |
|--|--------------------------------|------------------|-------------------|---|--------------------------------|
| Tracer | | | | | |
| Helium | He | 4.0 | 106 ^a | - | 1% |
| Difluoromethane | CF ₂ H ₂ | 52.0 | 0.47 ^b | 0.21 ^c | 100 ppm |

^a Measured at 25 oC (Battino, W.E.; Wilcock, R.J. Low-pressure solubility of gases in liquid water. *Chemical Reviews* 1977, 77, 219--262)..

^b Measured in this study for distilled water at 22.5 – 24.1°C.

^c Measured at 25 °C (Worksafe Australia, *National Industrial Chemicals Notification and Assessment Scheme, Difluoromethane*, NA/563, Sydney, Australia, 1988).

[00030] Hydrologists measuring water in the vadose zone have used carbon dioxide (Brusseau, M.L.; Popovicova, J.; Silva, J.A.K. Characterizing gas-water interfacial and bulk-water partitioning for gas-phase transport of organic contaminants in unsaturated porous media. *Environmental Science & Technology* 1997, 31, 1645--1649), bromochlorodifluoromethane (Deeds, N.E.; Pope, G.A.; Mckinney, D.C. Vadose zone characterization at a contaminated field site using partitioning interwell tracer technology. *Environmental Science & Technology* 1999, 33, 2745--2751), dibromodifluormethane (Nelson, N.T.; Brusseau, M.L.; Carlson, T.D.; Costanza, M.S.; Young, M.H.; Johnson, G.R.; Wierenga, P.J. A gas-phase partitioning tracer method for the in situ measurement of soil-water content. *Water Resources Research* 1999, 35, 3699--3707), and difluoromethane (Deeds, N.E.; McKinney, D.C.; Pope, G.A.; Whitely Jr., G.A. Difluoromethane as partitioning tracer to estimate vadose water saturations. *Journal of Environmental Engineering* 1999, 125, 630--633) as partitioning tracers. Partitioning tracers may include

(1) halogenated aliphatic compounds, such as bromochlorodifluoromethane, dibromodifluoromethane, difluoromethane, and 1,1,1-trifluoroethane; (2) weakly acidic and basic gases, such as carbon dioxide and ammonia; and (3) polar organic compounds (i.e., compounds containing oxygen or nitrogen), such as ketones, aldehydes, ethers, and amines. These compounds should have relatively small affinity for mineral surfaces, soil organic matter, and the gas-water interface. Difluoromethane was used in the experiments because it appears to be the most suitable of the above partitioning tracers for landfill applications. Bromochlorodifluoromethane and dibromodifluoromethane were not chosen because they might be reductively dehalogenated by anaerobic microorganisms such as methanogens and sulfate reducers, as has been observed for other chlorinated and brominated aliphatics (Belay, N.; Daniels, L. Production of ethane, ethylene, and acetylene from halogenated hydrocarbons by methanogenic bacteria. *Applied Environmental Microbiology* 1987, 53, 1604-1610; Sonier, D.N. ; Duran, N.L.; Smith, G.B. Dechlorination of trichlorofluoromethane (CFC-11) by sulfate-reducing bacteria from an aquifer contaminated with halogenated aliphatic compounds. *Applied Environmental Microbiology* 1994, 60, 4567-4572). In contrast, fluorinated compounds such as difluoromethane are less likely to undergo reductive dehalogenation reactions due to the high carbon-fluorine bond energies (Key, B.D.; Howell, R.D.; Criddle, C.S. Fluorinated organics in the biosphere. *Environmental Science & Technology* 1997, 31, 2445-2454). Direct reductive defluorination is difficult and is rarely observed (Key, B.D.; Howell, R.D.; Criddle, C.S. Fluorinated organics in the biosphere. *Environmental Science & Technology* 1997, 31, 2445-2454; Visscher, P.T.; Culbertson, C.W.; Oremland, R.S. Degradation of

trifluoroacetate in oxic and anoxic sediments. *Nature* 1994, 369, 729-731). Indirect defluorination, which occurs via reductive dechlorination or debromination followed by β - or α -elimination and hydrolysis to remove fluoride, is more common (Krone, U.E.; Thauer, R.K. Dehalogenation of Trichlorofluoromethane (CFC-11) by *Methanosarcina barkeri*. *FEMS Microbiological Letters* 1992, 90, 201-204; Krone, U.E.; Thauer, R.K.; Hogenkamp, H.P.C.; Steinbach, K. Reductive formation of carbon monoxide from CCl_4 and freons 11, 12, and 13 catalyzed by corrinoids. *Biochemistry* 1991, 30, 2713-2719; Gorsky, B.H.; Cascorbi, H.F. Halothane hepatotoxicity and fluoride production in mice and rats. *Anesthesiology* 1979, 50, 123-125). However, indirect reductive defluorination is not possible for difluoromethane since the reaction requires the presence of a chlorine or bromine substituent on the same or an adjacent carbon atom (Krone, U.E.; Thauer, R.K.; Hogenkamp, H.P.C.; Steinbach, K. Reductive formation of carbon monoxide from CCl_4 and freons 11, 12, and 13 catalyzed by corrinoids. *Biochemistry* 1991, 30, 2713-2719), which is lacking in difluoromethane. Other reactions difluoromethane may undergo, such as oxidative degradation by hydroxyl radical (Key, B.D.; Howell, R.D.; Criddle, C.S. Fluorinated organics in the biosphere. *Environmental Science & Technology* 1997, 31, 2445-2454; Franklin, J. The Atmospheric Degradation and Impact of 1,1,1,2-Tetrafluoroethane (Hydrofluorocarbon 134a). *Chemosphere* 1993, 27, 1565-1601) or monooxygenase enzymes (Olson, M.J.; O'Gara, J.F.; Surbrook, S.E.Jr. Metabolism in vivo and in vitro of the refrigerant substitute 1,1,1,2-tetrafluoro-2-chloroethane. *Drug Metabolism and Disposition* 1991, 19, 1004-1011), are most likely insignificant in landfills. The inertness of difluoromethane, combined with its high affinity for water (due

to the strong electronegativity of the fluorine substituents), makes it a suitable partitioning tracer for landfill applications.

[00031] Difluoromethane is a refrigerant gas and is used in low temperature refrigeration units, such as air conditioners and industrial cooling processes (Worksafe Australia, *National Industrial Chemicals Notification and Assessment Scheme, Difluoromethane*, NA/563, Sydney, Australia, 1998). It has been introduced to replace ozone-depleting chlorofluorocarbons and has negligible ozone depleting potential. The properties of difluoromethane are shown in Table 1 above.

Measurement of Henry's Law Constant

[00032] The Henry's law constant for helium is well known and is reported in Table 1 above. While the influence of temperature and leachate composition will have some effect on K_H , because $K_H \approx 100$ small changes in the Henry's law constant should have a minimal impact on helium transport: helium has such a strong affinity for the gas phase, that partitioning into the water phase will have a negligible influence on helium's mean travel velocity.

[00033] The Henry's law constant for difluoromethane in clean water was determined to be $K_H = 0.59$ in a recent experimental study (Deeds, N.E.; McKinney, D.C.; Pope, G.A.; Whitely Jr., G.A. Difluoromethane as partitioning tracer to estimate vadose water saturations. *Journal of Environmental Engineering* 1999, 125, 630--633). Based on the chemical structure of difluoromethane and the ranges of chemical parameters for landfill leachate reported in a recent review (Christensen, T.H.; Kjeldsen, P.; Bjerg, P.L.; Jensen, D.L.; Christensen, J.B.; Baun, A.; Albrechtsen, H.-J.; Heron, G. Biogeochemistry of

landfill leachate plumes. *Applied Geochemistry* 2001, 16, 659--718), we believe that leachate composition should not have a significant influence on difluoromethane partitioning. Our experiments were conducted to determine K_H for distilled water and a landfill leachate collected from the Cherry Island Landfill in Wilmington, DE. The composition of this test leachate is shown in Table 2. The leachate was kept in an oxygen-free environment before the K_H measurements.

[00034] **Table 2.** Composition of landfill leachate.

| Parameter | Value |
|---|-------|
| pH | 8.14 |
| Specific conductivity ($\mu\text{S cm}^{-1}$) | 7,770 |
| Total suspended solids (mg/l) | 403 |
| Total dissolved solids (mg/l) | 4,190 |
| Total organic carbon, TOC (mg/l) | 265 |
| Biological oxygen demand, BOD ₅ (mg/l) | 68 |
| Chemical oxygen demand, COD (mg/l) | 963 |

[00035] The experimental procedure used to determine K_H was similar to that reported in an earlier study (Deeds, N.E.; McKinney, D.C.; Pope, G.A.; Whitely Jr., G.A.

Difluoromethane as partitioning tracer to estimate vadose water saturations. *Journal of Environmental Engineering* 1999, 125, 630--633). A jacketed glass column 60-cm long

and 5-cm in diameter (Ace Glass, Inc., Vineland, NJ) was packed with 50/70 silica sand ($d_{50} = 0.26$ mm, uniformity index = 1.186; U.S. Silica, IL) underwater using distilled water. The column was positioned vertically, and suction was applied to the bottom of the column to drain water from the porous medium. Gravimetric measurements were then used to determine the porosity of the sand column and the final water saturation of the system. This packing procedure ensured that the water was uniformly distributed in the porous medium.

[00036] A water bath and pump were used to recirculate water in the glass jacket surrounding the porous medium to maintain fluid and gas temperatures between 22.5 – 24.1°C during the experiments. Each gas tracer test was started by directing a gas mixture, helium and difluoromethane in a balance of nitrogen, from a compressed gas cylinder into the sand column. The tracer gases were introduced as a step-input into the porous medium. A low-flow mass flow controller (Model VCD 1000, Porter Instruments, Hatfield, PA) was used to maintain a constant mass flux through the column during each experiment. The gas leaving the column was sampled using a 1-ml gas sampling valve at time intervals that varied depending on the gas flow rate for each experiment. Tracer concentrations in the gas samples were quantified with a gas chromatograph (Model 8610C, SRI Instruments, Torrance, CA): tracers were separated using mol-sieve and silica gel packed columns and then detected with a thermal conductivity (helium) or flame ionization detector (difluoromethane). Each experiment was stopped when the tracer concentrations in the effluent from the porous medium equaled the influent concentrations. To eliminate any concern about the influence of mass transfer limitations on K_H measurements, six trials

were conducted over a wide range of gas velocities to assess whether gas velocity affected the measurements.

[00037] Three trials were performed to determine K_H for the leachate. The experimental procedures were modified slightly from those described above for distilled water. Here, the column was packed with dry sand, purged with nitrogen, and the leachate was flushed upward in the vertically-mounted column to displace the gas. Nitrogen was then injected into the top of the column to force the mobile water out of the column. This procedure allowed the column to be wetted with the leachate while under anaerobic conditions. Between experimental trials anaerobic conditions were maintained in the column to minimize reactions within the leachate that might alter its composition. The temperatures for the leachate tests ranged between 25.5 – 26.0°C

[00038] The Henry's law constant was determined in each of the above tests using the tracer breakthrough curves and the known porosity and water saturation for the porous medium. Time moment analysis was used to determine the mean tracer velocities; R_f was computed from eq. 1; and using known n and S_w , K_H was computed from eq. 3.

Water Measurements in Municipal Solid Waste

[00039] Five experiments were conducted to measure the volumetric water content of solid waste. Four different solid waste compositions were used for the experiments and are shown in Table 3.

[00040] **Table 3.** Composition and properties of experimental packings. Solid waste constituents are percent by mass.

| Constituent or Property | Packing #1 (Exp. 1) | Packing #1 (Exp. 2) | Packing #2 (Exp. 3) | Packing #3 (Exp. 4) | Packing #4 (Exp. 5) |
|--|------------------------|------------------------|------------------------|------------------------|------------------------|
| Yardwaste | 19.2 | 19.2 | 23.2 | 20.0 | 2.0 |
| Foodwaste | 25.8 | 25.8 | 29.4 | 42.9 | 0.0 |
| Paper | 39.4 | 39.4 | 15.8 | 0.0 | 16.0 |
| Plastic | 11.2 | 11.2 | 18.0 | 22.8 | 0.0 |
| Glass | 4.3 | 4.3 | 13.5 | 14.3 | 82.0 |
| Bulk Density, dry (g/cm ³) | 0.35 | 0.28 | 0.26 | 0.28 | 0.43 |
| Porosity ^a , n (-) | 0.80-0.82 | 0.82-0.91 | 0.69-0.78 | 0.78-0.84 | 0.67-0.69 |
| Volumetric Water Content, θ_w (-) | 0.31 | 0.19 | 0.18 | 0.10 | 0.06 |
| Water Saturation ^a , S_w (-) | 0.37-0.39 | 0.20-0.23 | 0.24-0.27 | 0.12-0.13 | 0.09 |
| Moisture Content, M_c | NA | 0.51 | 0.56 | 0.39 | 0.14 |

^a Measured by gas tracer tests.

NA = not available

[00041] The composition of packing #1 was selected to mimic the average composition of trash found in municipal solid waste landfills in Delaware (SCS Engineers, *Delaware Solid*

Waste Authority Characterization Study, 1997). The solid waste compositions of the remaining packings were altered to enable a wider range of θ_w for the experiments: the amount of paper, foodwaste, and yardwaste had a significant influence on θ_w for each packing.

[00042] The preparation of the solid waste was the same for all experiments. The solid waste components were cut or broken into small pieces and then soaked in a known mass of water. The waste was removed from the soaking solution, mechanically squeezed, and packed into the same glass column used for the K_H measurements. Gravimetric measurements of the soaking solution before the solid waste was added and after it was removed, and the weight of the water that was drained from the solid waste through mechanical squeezing were used to determine θ_w of the packed column. These measurements only accounted for the water that was added to the solid waste: water that was initially bound to the air-dry waste material was not included.

[00043] The wet-weight moisture content of the solid waste M_c (mass of water/wet mass of solid waste) was determined in experiments 2-5. After completing the PGTT tests, the solid waste was removed from the column, weighed, oven dried at 105.0 ± 1.0 °C for 24 h, and then weighed again. Combining these measurements with the gravimetric measurements described above, the moisture content of the solid waste was determined before water addition (initial M_c) and after the solid waste was packed into the column (final M_c).

[00044] The volumetric water contents and final moisture contents for each experiment are reported in Table 3 above. Volumetric water contents vary between experiments primarily because of the amount of liquid water retained by each packing, not because of the initial moisture associated with the air-dry waste. Dry bulk densities of the air-dry waste determined before water addition are also shown. These bulk densities are representative of lightly compacted solid waste, as they are somewhat smaller than bulk densities reported for normally compacted municipal waste in landfills (Tchobanoglous, G.; Theisen, H.; Vigil, S. *Integrated Solid Waste Management, Engineering Principles and Management Issues*, McGraw-Hill, Inc.: New York, 1993): $0.36 - 0.50 \text{ g/cm}^3$.

[00045] After packing each column, two or three PGTT measurements were made in each experiment following the same procedures described above for the K_H measurements. Time moment analyses were performed to determine mean tracer travel times, from which S_w (eq. 3) and n (eq. 5) were determined. Because only θ_w was determined through gravimetric measurements, for comparison purposes θ_w was computed from the PGTT measurements using $\theta_w = nS_w$.

RESULTS

Henry's Law Constant

[00046] The porosity and water saturation of the sand column used in the measurements for K_H were $n = 0.34$ and $S_w = 0.24$ respectively. Figure 1 shows a typical breakthrough curve from the six PGTTs in the system with distilled water. Helium breaks through much earlier than difluoromethane, although both tracers eventually reach the

injection concentration at late time. Using data from the six trials and following the analysis procedures outlined above, the Henry's law constant for difluoromethane was $K_H = 0.47 \pm 0.07$ CI (CI = 95% confidence interval). Although the interstitial gas velocity was varied from 2.1 m/day to 46.9 m/day in the six trials, there were no systematic changes in K_H as gas velocity increased. For this reason, it is unlikely that mass transfer limitations affected K_H measurements.

[00047] Three PGTT were conducted with landfill leachate to explore the influence of leachate composition on difluoromethane partitioning. The porosity and leachate saturation of the sand column were $n = 0.41$ and $S_w = 0.17$ respectively, while the average interstitial gas velocity used in the tracer tests was 25.2 m/day. The Henry's law constant for difluoromethane was $K_H = 0.57 \pm 0.09$ CI, which is 20% larger than that for distilled water. The increase in K_H may have been due to constituents in the leachate or temperature differences between K_H measurements in leachate and distilled water: mean leachate temperatures were approximately 2.5°C larger than those for distilled water. While further work is necessary to explain these data, in the measurements reported below for solid waste the Henry's law constant for difluoromethane was assumed to be $K_H = 0.47$, since distilled water was added to the solid waste to achieve different water contents. The impact of leachate composition and temperature on the Henry's law constant and their influence on field measurements is discussed further below.

Water Saturation in Municipal Solid Waste

[00048] Five experiments were conducted in four different solid waste packings to evaluate the utility of PGTT for measuring water. The results from these experiments are shown in Figure 2, where θ_w measured with PGTT are plotted versus gravimetric measurements. Volumetric water contents were determined over a wide range, $\theta_w = 0.06$ to $\theta_w = 0.31$, representing water saturations that ranged from $S_w = 0.09$ to $S_w = 0.39$. These water contents and water saturations were determined from measured water added to the air-dry waste; they do not account for the additional water contained within the waste components before liquid water addition. The initial moisture content of the solid waste in these experiments ranged from 0.1% (experiment 5) to 18.3% (experiment 2), while the final moisture content after adding water to the solid waste ranged from 14.5% (experiment 5) to 56.0% (experiment 3).

[00049] Errors in θ_w measurements using PGTT were at most 48%, with most less than 15%. There was no systematic bias in the measurements: the data fell evenly about the line of perfect fit shown in Figure 2. Thus, these PGTTs measured the free liquid water added to the air-dry waste with reasonable accuracy. On the other hand, the variation in measured θ_w for replicate tests for the same experiment was more significant than expected, and may be due to the relatively large interstitial gas velocities used in these experiments, which ranged from 6 to 39 m/day. While we observed no systematic errors associated with changes in gas velocity over this range in the K_H measurements, others measuring water in soils suggest that gas velocities be kept to less than approximately

1m/day to minimize errors associated with mass transfer limitations (Deeds, N.E.; McKinney, D.C.; Pope, G.A.; Whitely Jr., G.A. Difluoromethane as partitioning tracer to estimate vadose water saturations. *Journal of Environmental Engineering* 1999, 125, 630--633). The precision of water measurements may be improved if smaller gas velocities were used. Despite the significance of the random errors in these data, the results are encouraging and demonstrate that the PGTT is a promising technology for measuring water in solid waste.

Conclusion

Factors Affecting Henry's Law Constant

[00050] The Henry's law constant of the partitioning tracer is a critical parameter in the measurement of water with a PGTT. While the effect of leachate composition and a small temperature change (2.5°C) had a minor effect on K_H for the test leachate in this study, additional consideration of factors that might influence difluoromethane partitioning is warranted. A comprehensive critical review of Henry's law constants for organic compounds suggests that two of the most important factors that may influence difluoromethane partitioning into leachate are dissolved salts and temperature (Staudinger, J.; Roberts, P.V. A Critical review of Henry's Law constants for environmental applications. *Critical Reviews in Environmental Science and Technology*, 1996, 26, 205--297). Other factors, such as dissolved organic matter and suspended solids are important for hydrophobic compounds (high octanol/water partition coefficient), but should be of minor importance for difluoromethane.

[00051] Dissolved inorganic salts affect the fugacity of a compound in the water phase, but do not influence the fugacity in the gas phase. Therefore, we estimated the influence of dissolved salts on difluoromethane partitioning by estimating their effect on its water solubility, using a modified Setschenow equation (Schwarzenbach, R.P.; Gschwend, P.M.; Imboden, D.M. *Environmental Organic Chemistry*, John Wiley & Sons: New York, 1993)

$$K_{H,salt} = K_H \times 10^{K_S[salt]} \quad (8)$$

where K_H and $K_{H,salt}$ are Henry's law constants for pure water and water containing dissolved salts, respectively, and K_S is the Setschenow constant or salting constant, in M^{-1} . The salt effect is compound-dependent and somewhat affected by the ionic species present in solution (Schwarzenbach, R.P.; Gschwend, P.M.; Imboden, D.M. *Environmental Organic Chemistry*, John Wiley & Sons: New York, 1993). Since to the best of our knowledge the Setschenow constant for difluoromethane is unknown, we used a conservative K_S value of 0.3, the largest value reported for halogenated aliphatic compounds in seawater (Schwarzenbach, R.P.; Gschwend, P.M.; Imboden, D.M. *Environmental Organic Chemistry*, John Wiley & Sons: New York, 1993). Because the composition of ionic species in landfill leachate vary widely (Christensen, T.H.; Kjeldsen, P.; Bjerg, P.L.; Jensen, D.L.; Christensen, J.B.; Baun, A.; Albrechtsen, H.-J.; Heron, G. Biogeochemistry of landfill leachate plumes. *Applied Geochemistry* 2001, 16, 659--718), we performed the calculation for three salts consisting of mono- and di-valent ions commonly found in leachate (Christensen, T.H.; Kjeldsen, P.; Bjerg, P.L.; Jensen, D.L.; Christensen, J.B.; Baun, A.; Albrechtsen, H.-J.; Heron, G. Biogeochemistry of landfill

leachate plumes. *Applied Geochemistry* 2001, 16, 659--718). To simplify the analysis, we assumed that only a single salt was found in the leachate at any time. A wide range of salt concentrations were examined to bracket the observed range of electrical conductivities for leachate (Christensen, T.H.; Kjeldsen, P.; Bjerg, P.L.; Jensen, D.L.; Christensen, J.B.; Baun, A.; Albrechtsen, H.-J.; Heron, G. Biogeochemistry of landfill leachate plumes. *Applied Geochemistry* 2001, 16, 659--718). The salt concentrations for the Setschenow equation were obtained at a specified electrical conductivity for the leachate using (Tchobanoglous, G.; Schroeder, E.D. *Water Quality*, Addison-Wesley: Reading, MA, 1987)

$$EC \approx \sum_i (C_i \times f_i) \quad (9)$$

where EC is electrical conductivity in $\mu\text{S}/\text{cm}$, C_i is ion concentration in meq/L , and f_i is the conductivity factor in $\mu\text{S}\cdot\text{L}/\text{cm}\cdot\text{meq}$. The f_i values for Na^+ , K^+ , Mg^{2+} , Cl^- , and SO_4^{2-} are 48.9, 72.0, 46.6, 75.9, and 73.9, respectively (Tchobanoglous, G.; Schroeder, E.D. *Water Quality*, Addison-Wesley: Reading, MA, 1987).

[00052] Figure 3 shows the salt effect on the Henry's law constant for difluoromethane when the salt is NaCl , MgSO_4 , or K_2SO_4 . The salt effect is largest for NaCl , although the change in K_H is less than 20% even for the highest leachate conductivity reported (Christensen, T.H.; Kjeldsen, P.; Bjerg, P.L.; Jensen, D.L.; Christensen, J.B.; Baun, A.; Albrechtsen, H.-J.; Heron, G. Biogeochemistry of landfill leachate plumes. *Applied Geochemistry* 2001, 16, 659--718). Because in our calculations all conductivity was attributed to a single salt (NaCl , MgSO_4 , or K_2SO_4), we expect that the change in Henry's

law constant for an actual leachate with a given conductivity should fall between those reported for NaCl and K₂SO₄ in Figure 3.

[00053] Temperature is also expected to influence difluoromethane partitioning into water. The solid waste experiments in this study were conducted between 25.5 – 26.3°C, while landfill temperatures may vary between 10 – 60 °C, depending on climatic conditions and landfill properties. While the temperature dependence of Henry’s law constant for difluoromethane has not been reported, changes in partitioning with temperature were reported for a similar compound, fluoromethane (Staudinger, J.; Roberts, P.V. A critical compilation of Henry's law constant temperature dependence relations for organic compounds in dilute aqueous solutions. *Chemosphere* 2001, 44, 561--576). Here, K_H increased by approximately 20% for every 10°C increase in temperature, and similar variations are expected for difluoromethane. Fortunately, temperature can easily be measured in landfill regions where PGTTs are conducted. If the temperature dependence of K_H for difluoromethane is determined in future research, corrections may then be used to account for the effect of temperature on difluoromethane partitioning in field tests.

[00054] It is important to evaluate the influence of errors in K_H associated with dissolved salts or temperature on water saturation measurements. A propagation of error analysis was used to determine the systematic bias in S_w due to a systematic error in K_H , and the results are shown in Figure 4. Relative errors in S_w are always less than or equal to relative errors in K_H , with errors in S_w decreasing as water saturation increases. Since for difluoromethane the error in K_H due to dissolved salts is expected to be less than 20%,

errors in S_w should also be 20% or less. The effect of temperature on difluoromethane partitioning is less certain. However, if the error in K_H for difluoromethane is similar to that of fluoromethane and if temperature variations on the order of 10°C are not accounted for in field measurements, errors in K_H are also expected to be on the order of 20%, resulting in S_w errors of 20% or less. These results suggest that both dissolved salts and temperature will contribute to water saturation measurement errors on the order of 20% or less. More accurate measurements can be achieved if the leachate has moderate to low salinity, and if the temperature that the PGTT is conducted at in the field is measured and used to select the appropriate K_H .

Moisture Content Versus Volumetric Water Content or Water Saturation

[00055] Moisture content is the most common measurement of water within the solid waste industry. One reason this measure is so frequently used is that it is simple and only involves gravimetric measurements. On the other hand, PGTTs determine the water saturation for open systems in the field, or both the water saturation and the volumetric water content for closed systems in the laboratory. We demonstrated how PGTTs determine with reasonable accuracy the volumetric water content associated with liquid water added to air-dry waste. While it may be possible for PGTTs to determine all water contained within the pores of solid waste, the tests in this study only determined the liquid water that was added to the waste. Water contained in the initial air-dry waste was not measured.

[00056] While moisture content will in general increase with increasing water saturation, see for example the data shown in Table 3 above, it may be impossible to establish a quantitative relationship between the two. Because the moisture content is a gravimetric measurement, it is dependent on the volume of water in the solid waste sample, the density of solid waste components, and the gas-filled volume of the sample. On the other hand, water saturation is a function of the volume of water and the gas-filled volume of the sample. While approximate relationships may be developed to relate moisture content and water saturation for specific types of solid waste, it is unlikely that quantitative relationships can be found.

[00057] Partitioning gas tracer tests are a promising technology for measuring water within landfills. Changes in landfill properties have a minor influence on this technology (e.g., porosity, leachate salinity), and PGTTs are capable of measuring the water saturation in small or large volumes of solid waste, depending on the position of the tracer injection and extraction points. Such tests are useful to determine relative differences in moisture in various regions of a landfill, thus enabling operators to determine where to add additional water.

[00058] All the references described above are incorporated by reference in its entirety for all useful purposes.

[00059] While there is shown and described certain specific structures embodying the invention, it will be manifest to those skilled in the art that various modifications and rearrangements of the parts may be made without departing from the spirit and scope of the

underlying inventive concept and that the same is not limited to the particular forms herein shown and described.

We claim:

1. A process to determine the amount of water needed in a landfill which comprises measuring water within solid waste of a landfill by injecting two gas tracers within solid waste to measure the fraction of the void space filled with water, and then determining the amount of water in the landfill wherein one tracer is conservative and does not react with solids or liquids, while the second gas tracer partitions into the water and is separated from the conservative tracer during transport.

ABSTRACT

[00060] A key component in the operation of almost all bioreactor landfills is the addition of water to maintain optimal moisture conditions. To determine how much water is needed and where to add it in situ methods are required to measure water within solid waste. We found that the transport behavior of two gas tracers within solid waste is used to measure the fraction of the void space filled with water. One tracer is conservative and does not react with solids or liquids, while a second partitions into the water and is separated from the conservative tracer during transport.

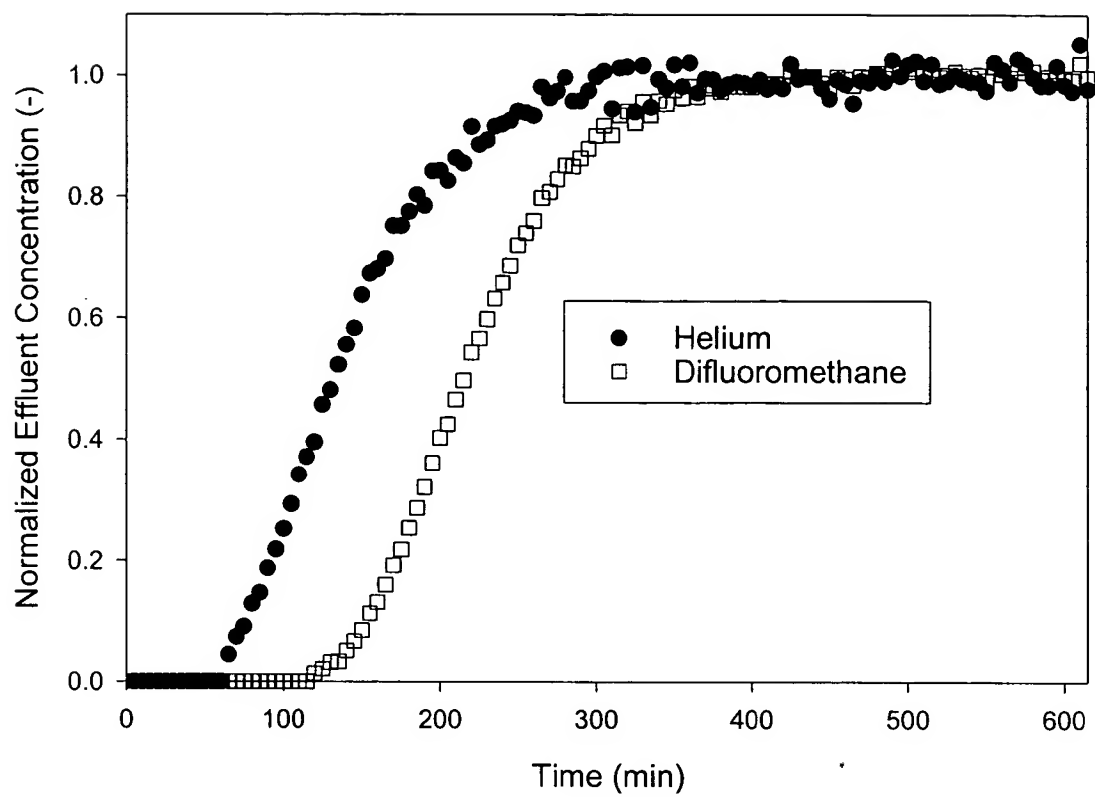


Figure 1

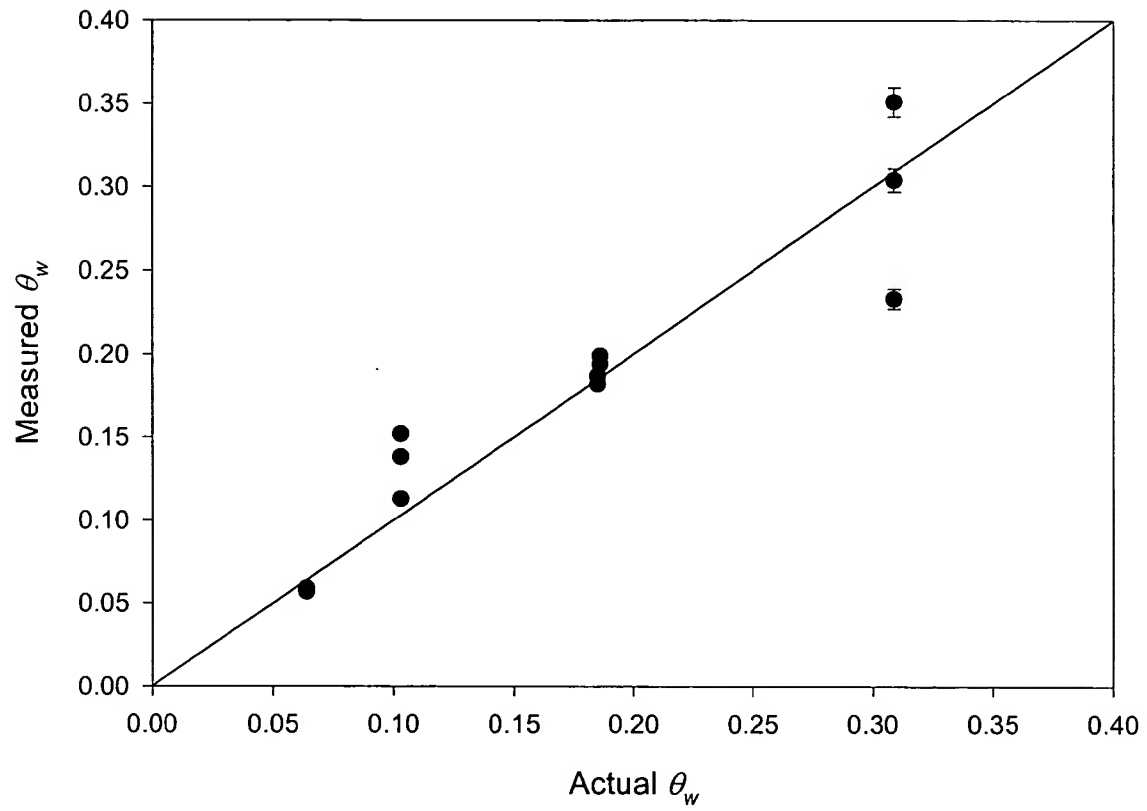


Figure 2

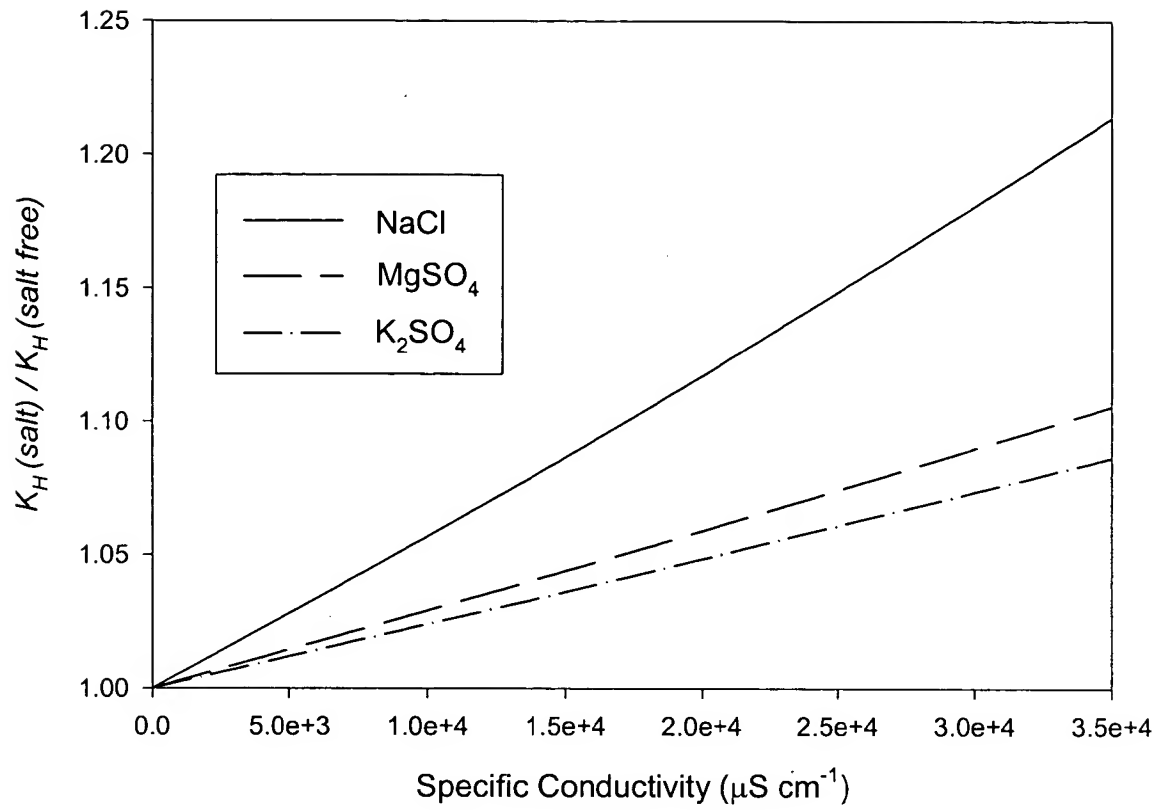


Figure 3

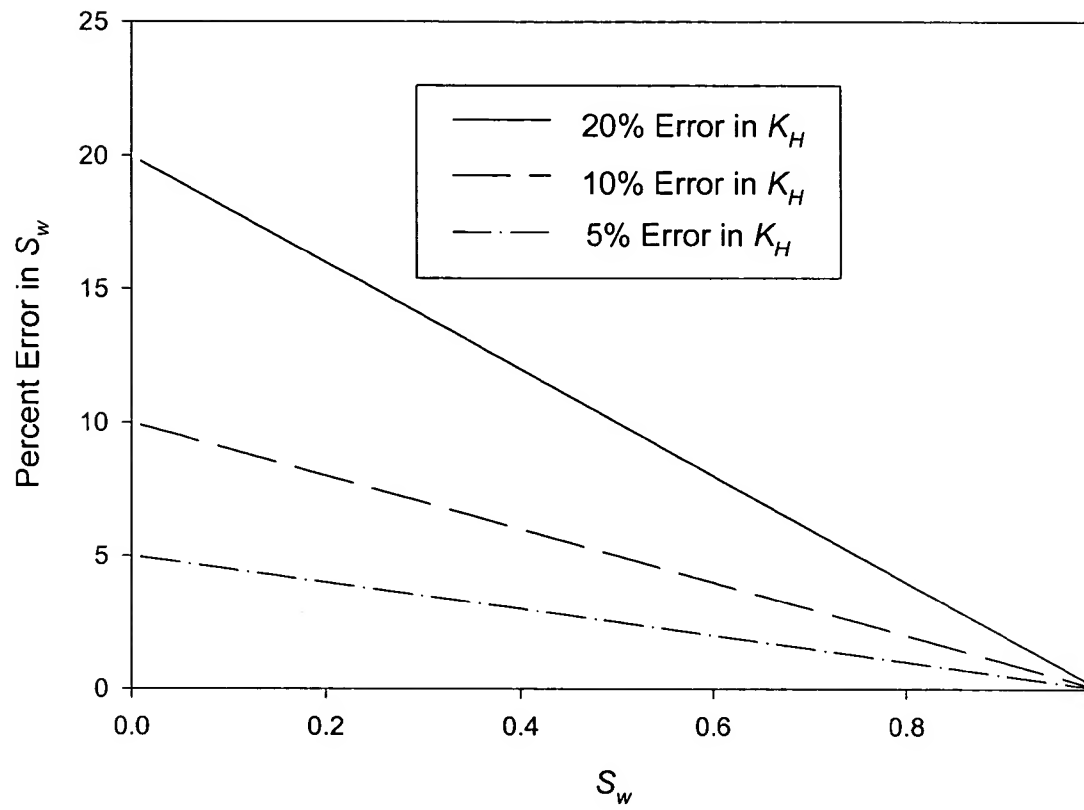


Figure 4

Application Data Sheet

Application Information

| | |
|----------------------------------|---|
| Application Type:: | Provisional |
| Subject Matter:: | Utility |
| Suggested Group Art Unit:: | N/A |
| CD-ROM or CD-R?:: | None |
| Sequence submission?:: | None |
| Computer Readable Form (CRF)?:: | No |
| Title:: | PARTITIONING GAS TRACER TESTS FOR MEASUREMENT OF WATER IN MUNICIPAL SOLID WASTE |
| Attorney Docket Number:: | 00131-00345-US |
| Request for Early Publication?:: | No |
| Request for Non-Publication?:: | No |
| Small Entity?:: | Yes |
| Petition included?:: | No |
| Secrecy Order in Parent Appl.?:: | No |

Applicant Information

| | |
|---|------------------|
| Applicant Authority Type:: | Inventor |
| Primary Citizenship Country:: | US |
| Status:: | Full Capacity |
| Given Name:: | Paul |
| Family Name:: | Imhoff |
| City of Residence:: | Newark |
| State or Province of Residence:: | DE |
| Country of Residence:: | US |
| Street of mailing address:: | 202 MacDuff Road |
| City of mailing address:: | Newark |
| State or Province of mailing address:: | DE |
| Postal or Zip Code of mailing address:: | 19711 |

| | |
|---|---------------------------|
| Applicant Authority Type:: | Inventor |
| Primary Citizenship Country:: | Taiwan, Republic of China |
| Status:: | Full Capacity |
| Given Name:: | Pei |
| Family Name:: | Chiu |
| City of Residence:: | Hockessin |
| State or Province of Residence:: | DE |
| Country of Residence:: | US |
| Street of mailing address:: | 201 Eileens Way |
| City of mailing address:: | Hockessin |
| State or Province of mailing address:: | DE |
| Postal or Zip Code of mailing address:: | 19707 |

Correspondence Information

| | |
|----------------------------------|-------|
| Correspondence Customer Number:: | 23416 |
|----------------------------------|-------|

Representative Information

| | |
|----------------------------------|-------|
| Representative Customer Number:: | 23416 |
|----------------------------------|-------|